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"FUNDAMENTAL STUDY OF DENSE-FLUID DETONATION"

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SUMMARY

(1) TECHNICAL PROBLEM

We are investigating atomistic mathematical models of energy transferred in condensed media. We wish to obtain a fundamental understanding of the interaction of compressive waves with intermolecular and intramolecular energies, leading to the initiation of detonation.

(2) GENERAL METHODOLOGY

We analyze quasistatic compression by comparing equilibrium statistical-mechanical calculations with the results of equilibrium Newtonian molecular dynamics simulations. We are developing and solving nonequilibrium, equations of motion to describe the rapid compression of microscopic polyatomic systems. We emphasize the flow of energy among the molecular degrees of freedom excited by the compression process.

(3) TECHNICAL RESULTS

We have determined the atomistic pair distribution function for planar crystals undergoing both uniaxial and hydrostatic compression. We have compared these distributions to the predictions of the Pastine-Kamlet-Jacobs model.

We have simulated bimolecular collisions of triatomic and hexatomic planar molecules (with hexanitrobenzene in mind). We analyze the normal-mode vibrations before and after collision and observe the transfer of energy among the translational, rotational, and vibrational modes.

(4) FURTHER RESEARCH IMPLICATIONS

The simulations of rapid deformation will be extended to larger molecules, in three dimensions, and will be made consistent with macroscopic thermodynamics. These extensions require equations of motion incorporating a nonequilibrium inhomogeneous deformation satisfying the adiabatic first law $\dot{E} \cong -VP:\nabla u$.

I. INTRODUCTION

Shock and detonation waves involve atomic-scale processes which are imperfectly understood and hard to measure. The systems contain too many atoms for an accurate quantum-mechanical treatment. Classical calculations can deal with systems of hundreds or thousands of interacting atoms, over hundreds or thousands of vibrational periods.

To evaluate the utility of the microscopic approach we have embarked on a program to develop and apply modern computational methods to the nonequilibrium dynamical processes responsible for explosive initiation. A detailed microscopic view is necessitated by the violent nonequilibrium nature of shock compression. Simulations show that the intrinsic width of a shock front is only a few atomic diameters.[1] Thus the usual concept of equilibrium temperature, with Arrhenius kinetics, is unlikely to provide an understanding of the initiation of chemical reactions.[2] To achieve understanding of initiation detailed studies of rapid nonequilibrium intermolecular and intramolecular energy transfer must be carried out and analyzed.

Over the past several years there has been considerable progress in treating the deformation of simple monatomic fluids and solids. The techniques developed have been tested by intercomparison with experimental data and with less-efficient older simulation techniques.[3] The irreversible heating associated with rapid viscons and plastic deformation has been avoided by developing isothermal equations of motion.[4] These equations constrain the second moment of the velocity distribution, $\langle (v-\langle v\rangle^2\rangle$, to a fixed value. Analogous developments for treating diffusion and conduction stem from this same foundation.[5]

These new methods have not been applied to flexible polyatomic molecules. In order to carry out this generalization we have analyzed both quasistatic and rapid deformations of monatomic crystals (Section II), the rotational and colli-

sional transfer of polyatomic molecular energies (Section III), and the thermodynamic consistency of rapid polyatomic deformation (Section IV). During the remainder of this contract we will combine the energy transfer and deformation techniques to study a model of solid hexanitrobenzene.

II. DEFORMATION OF MONATOMIC SOLIDS

In a series of studies we have characterized the compression of simple fluids and solids. We recently carried out a detailed study of equilibrium pair distribution functions in deformed two-dimensional crystals.[6] Both Hooke's-Law and Lennard-Jones forces were used. The pair distributions, obtained by integrating the quasiharmonic canonical probability density, differ from approximate theoretical treatments in two ways. First, contributions from all normal-mode vibrations are included. Second, reaction-rate contributions from all diatomic orientations are included. For these reasons the reaction rates follow neither the simple Gruneisen density dependence nor Arrhenius kinetics. Even under quasistatic conditions, uniaxial compression generally yields significantly higher collision (or reaction) rates than does the corresponding hydrostatic compression.

Earlier deformation studies, under both shockwave and homogeneous conditions, have demonstrated the utility of incorporating the macroscopic velocity gradient ∇u directly into microscopic equations of motions. The shockwave studies emphasized the nonequilibrium velocity distribution in the shock-front. Shockwave structure, bulk and shear viscosities, and solid-phase high-strain-rate yield stengths[7] have all been determined in this way. Adiabatic deformation can be modeled by adding an extra contribution to the atomic velocities, $\dot{q} = q \cdot \nabla u$, and a corresponding force $\dot{p} = -\nabla u \cdot p$. The two modifications lead to the thermodynamic identity

$$\dot{E} = -VP : \nabla u,$$

where E is internal energy and P is the pressure tensor. This adiabatic deformation can be made isothermal instead by including an additional collective force $-\zeta p$, with ζ chosen to keep $\langle p^2/m \rangle$ constant.

III. ENERGY TRANSFER IN POLYATOMIC MOLECULES

The simplest polyatomic molecule exhibiting energy transfer is a planar triatomic molecule, with three vibrational degrees of freedom. In this case the two degenerate vibrational modes are coupled by Coriolis forces. Thus rotation of the molecule, even very slowly, leads to a geometric coupling of two vibrational amplitudes.

Regular hexatomic planar molecules have nine vibrational degrees of freedom, with four pairs of degenerate modes in addition to the symmetric breathing mode. At reasonable rotational velocities the coupling among the four pairs is negligible. Even at vanishing velocities Cordiolis coupling again causes the cycling back and forth between degenerate mode amplitudes.

We have simulated bimolecular collisions of both triangular and hexagonal planar molecules, have analyzed their normal-mode vibrations throughout the collision process, and have observed energy transfer among all the translational, rotational, and vibrational degrees of freedom. Presently we are characterizing the energy distribution during a homogeneous compression.

IV. THERMODYNAMICS OF RAPID DEFORMATION

The virial theorem relates the pressure tensor to interatomic forces. In the familiar monatomic form[8] each Newton's equation of motion is multiplied by the corresponding particle coordinate, summed and averaged, to give

$$\sum \sum r_i F_{ij} - VP = \sum \frac{d}{dt}(m r \dot{r})_i - (m r \ddot{r})_i .$$

which is equivalent to

$$PV = NkTI + \sum r_{ij} F_{ij}$$

where N is the number of atoms in the volume pairs. For polyatomic molecules it is convenient to multiply each atom's equation of motion by the center of mass coordinate for its molecule. The force terms in each molecule cancel, with the result:

$$PV = NkTI + \sum R_{ij} F_{ij}$$

where N is now the number of _molecules_ and F_{ij} is the vector sum of forces of all atoms in molecule I due to atoms in molecule J.

Now consider two kinds of adiabatic deformation. In "atomic" deformation each atom undergoes a displacement proportional to its location

$$\dot{r} = r \cdot \nabla u$$

and a corresponding force

$$\dot{p} = -p \cdot \nabla u .$$

The adiabatic first-law identity, $\dot{E} = -VP \cdot \nabla u$, follows. In "molecular" deformation each atom undergoes a displacment proportional to the center-of-mass coordinate R:

$$\dot{r} = R \cdot \nabla u$$

as well as a corresponding force

$$\dot{p} = -P(\tfrac{m}{M}) \cdot \nabla u .$$

The identify $\dot{E} = -PV : \nabla u$ again follows, provided that P is the "molecular" pressure.

It is presently unknown which of these formulations best describes adiabatic polyatomic deformation. We will apply both methods to rapid deformation of hexagonal molecules in our energy transfer simulations in the coming year.

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